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Effect of dissolved LiCl on the ionic liquid–Au(111) electrical double layer structure†

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The electrical double layer at ionic liquid (IL)–Au(111) interfaces is composed of alternating ion layers. Interfacial layering is markedly weaker when small amounts of LiCl are dissolved in the IL for all potential between −2.0 V and +2.0 V (*vs.* Pt). This means that models developed for pure IL electrical double layers may not be valid when solutes are present.

Ionic liquid (IL) electrochemical research is complicated by the absence of a comprehensive model for the structure of the electrified solid–IL interface.[1] While the electrical double layer is well-described for aqueous systems,[2–4] descriptions for IL systems are still developing,[5,6] and to date have focussed on pure liquids; the effect of dissolved solutes on interfacial IL nanostructure and the double layer has received scant attention.[7] In this paper the effect of dissolved LiCl on IL interfacial nanostructure at an electrode surface as a function of potential is probed. These results will enhance our understanding of the electrical double layer in IL systems. The system examined models some of the more promising IL based electrochemical applications, including electrodeposition[8] and Li-batteries,[9] where adsorption of ions to the solid surfaces, and the near surface liquid nanostructure, play key roles in determining performance.

The IL–electrode interface is more complex than aqueous systems.[10] For instance, solvent–solvent interactions are considerably different in ILs. Because ILs are pure liquid electrolytes, the ionic atmosphere is not diluted by neutral solvent molecules. This leads to highly effective charge screening in ILs, with calculated Debye lengths of order of the size of individual ions. Moreover, unlike inorganic electrolytes, the electrostatic charge is usually not localized on one atom and so the system cannot be modelled as a continuum of spherical point charges. In general, IL ions are large and asymmetric, with the charge delocalized over one or more functional groups. Compared to inorganic salts, this changes the cohesive interactions in ILs by both weakening electrostatic attractions/repulsions and introducing the potential for other types of ion–ion interactions common to molecular solvents[11] or surfactant mesophases,[2] *e.g.* H-bonding[12] or solvophobic[13] interactions.

Compared to aqueous electrolytes, ion–surface interactions are also considerably different in ILs. Many computational papers have shown that ion–surface interactions are strong in ILs and are driven by electrostatic attractions (*via* charged groups) or van der Waals forces (*via* uncharged groups) between ions and the surface respectively.[6,14–17] Notably, because the concentration of ions is high and relatively uniform in ILs, the ion–surface interactions are not strong enough to induce distinct regions of ion excess and ion depletion close to the interface analogous to Stern and diffuse layers in classical theories for aqueous electrolytes. Instead, experimental measurements reveal ILs display ion layering at solid surfaces,[18–22] including at charged electrode interfaces.[10,23–27] In some respects, this is reminiscent of solvation layers for molecular liquids[2] or simple ABABA-type ion layering in pure molten inorganic salts at solid interfaces.[28,29]

IL surface layering depends on both surface-specific and bulk factors.[21] The bulk contribution is derived from the IL ion amphiphilicity, which promotes self-assembly of charged and uncharged molecular groups, often in sponge-like nanostructures;[30,31] the interface acts to orient and align this nanostructure into layers. Surface-specific effects refer to the competition between overscreening and lattice saturation. In Kornyshev's model,[5] the ions arrange into layers of counter ions, co-ions, counter ions *etc.*, where each successive layer away from the interface forms a net negative (or positive) plane of charge that overcompensates the potential of the underlying layer. If the electrode is sufficiently polarized, multiple layers of the same ion type may be required to quench the electrode's surface charge.

In this manuscript we examine how the structure of the IL–electrode interface changes with 0.05 wt% dissolved salt (LiCl) using Atomic Force Microscopy (AFM) force curve measurements. Dissolved solutes have a strong influence on the double layer structure in aqueous systems[2] and are known to alter the interfacial (electro-)chemistry of ILs even at very low concentrations.[32] We present force curve data for three Au(111) surface electrode potentials – open circuit potential

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(ocp), −2.0 V, and +2.0 V (all *versus* Pt reference electrode) – and compare the results to our previous investigation[26] with the same IL (1-hexyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [HMIm]FAP) at the pure IL–Au(111) electrode interface.

Fig. 1A–C shows force *vs.* separation profiles for an AFM tip completely immersed in [HMIm]FAP + 0.05 wt% LiCl (blue) approaching the Au(111) electrode surface at three different surface electrode potentials; A: ocp, B: −2.0 V, C: +2.0 V (*versus* a Pt quasi-reference electrode). Corresponding data for pure [HMIm]FAP (green) is also presented.[26] Comparison between the data sets allows the effect of LiCl addition on IL interfacial structure to be commented upon, as it highlights differences both as a function of distance from Au(111) interface (intra-profile) and surface electrode potential (between profiles). As results for the pure [HMIm]FAP have already been discussed,[26] the focus of this manuscript is the [HMIm]FAP + 0.05 wt% LiCl data.

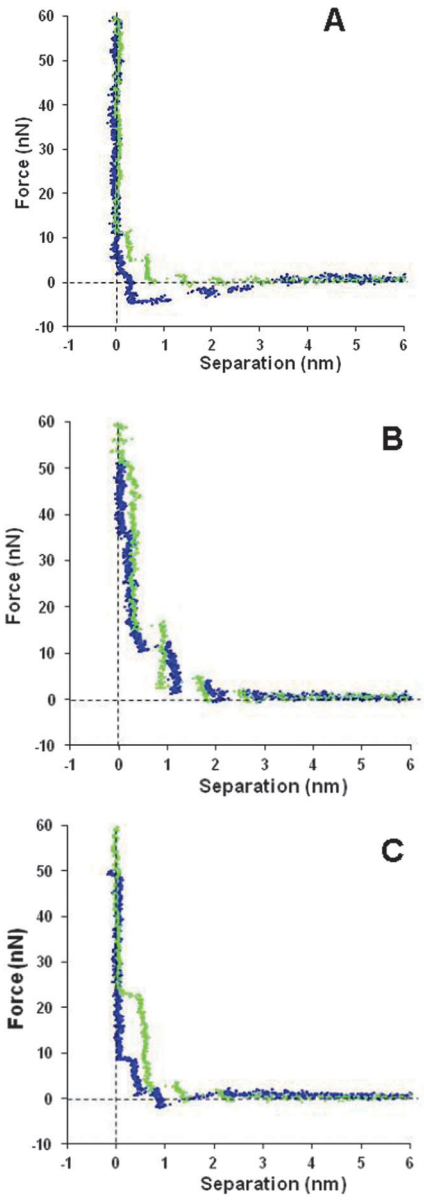

Fig. 1 Typical force *versus* distance profiles for an AFM tip approaching a Au(111) surface at different surface electrode potentials in [HMIm]FAP + 0.05 wt% LiCl (blue) and pure [HMIm]FAP (green). Data for (A) Open Circuit Potential (ocp, −0.11 V) (B) −2.0 V (*vs.* Pt) (C) +2.0 V (*vs.* Pt).

The form of the force curve data in the presence and absence of LiCl is similar, with stepwise profiles recorded as the tip pushes up against, and then ruptures, successive ion layers. This indicates a layered ion arrangement at the Au(111) interface. However, at all potentials investigated, the addition of LiCl reduces the force required to rupture near-surface layers, implying that near surface ionic liquid structure is weakened. This is most notable at ocp, where the interaction between the surface and the AFM tip changes from repulsive in the absence of electrolyte, to attractive when 0.05 wt% LiCl is present. Applying a potential to the surface increases the strength of surface layering, and repulsive forces are measured again, but the rupture force for layers is always lower than in the absence of electrolyte. One consequence of the reduced strength of interfacial layering is that the steps in the force profile are less clear, and the spacing between steps is not as consistent as for the pure liquid. Nonetheless, inferences about the effect of added LiCl on interfacial structure may still be drawn.

For [HMIm]FAP + 0.05 wt% LiCl at ocp, as the tip moves towards the surface an attractive force is measured from 3.5 nm to 0.3 nm. The force then becomes repulsive, as the tip pushes against the layer in contact with the surface until a force of ~2.5 nN is reached, and this layer is ruptured. Even though the tip–surface interaction is attractive, the presence of steps in the force profile confirm that a layered interfacial structure is retained. The spacing between steps in the force data is considerably more scattered (±0.2 nm) in the presence of LiCl than for pure [HMIm]FAP. This finding, in conjunction with weakened forces, suggests that dissolved Li^+ and/or Cl^- ions weaken the IL's interfacial layering.

Comparison of the step positions in Fig. 1A elucidate how IL interfacial structure changes at ocp with added LiCl. The presence of steps at ~0.3 nm and ~0.85 nm in both the presence and absence of LiCl indicates that the IL ion arrangement is similar in the first two ion layers. These dimensions approximately correspond to the size of the $[HMIm]^+$ cations (~0.3 nm) and ion pair (~0.85 nm). This indicates that the counter-ion (cation) is enriched and the co-ion (anion) is depleted (repelled) at the surface. This surface layer is weakly bound, and the AFM tip is able to displace it and move into contact with the Au(111) surface. Although there are steps in the force curve at wider separations, they are difficult to detect because of the attractive interaction and cannot readily be associated with the ion dimensions, consistent with weak structure.

The AFM data for negative (−2.0 V: Fig. 1B) and positive polarizations (+2.0 V: Fig. 1C) are quite different compared to ocp. At both positive and negative potentials, the forces are repulsive in every instance. This means that the interfacial structure is stronger at these potentials than at ocp, consistent with previous results for pure ILs as potential is raised.[23,26] However, the layer rupture forces are reduced compared to those obtained for the pure liquid at the same potentials, meaning that surface structure is reduced. Thus, there are two competing effects: LiCl acting to reduce interfacial structure

and the increased surface electrode potential favouring it. Steps consistent with cation-enriched (~0.3 nm) and anion-enriched layers (~0.5 nm) are detected nearest the surface, at negative and positive surface electrode potentials respectively. This suggests the ion layer flanking the interface quenches the surface charge. The innermost steps appear slightly smaller than for pure [HMIm]FAP. This may be due to increased local concentration of Li^+ cations or Cl^- anions in these layers reducing the average step size. Force data was also obtained at +1.0 V and −1.0 V but the data was much less consistent in terms of both the step spacing and push through forces, so is not presented. This variability is consistent with weaker interfacial structure.

At this stage, the precise mechanism by which LiCl reduces interfacial structure is unclear. At 0.05 wt%, the mole ratio of LiCl to [HMIm]FAP is 1 : 138, which would seem to be too low to markedly change the bulk IL nanostructure, and consequently the surface structure. *i.e.* it is unlikely that LiCl is evenly distributed throughout the liquid, but rather is concentrated at the surface. This seems probable, as both the Li^+ cation and the Cl^- anion are smaller and harder than their IL counterparts, so will be more strongly attracted to a polarized surface. Enrichment of LiCl near the electrode surface could reduce the interfacial forces in three ways. Firstly, the near-surface LiCl concentration could be sufficiently high to markedly reduce the strength of interfacial IL nanostructure, perhaps by swelling and weakening the electrostatic domains. Alternatively, interfacial LiCl could change the IL's Hamaker constant in the vicinity of the surface, such that a stronger attraction results at close separations. This need not necessarily lead to a reduction in near surface nanostructure, but cannot be ruled out. Finally, and in our view most likely, either the Li^+ or Cl^- is preferentially adsorbed to the electrode surface (depending on potential), impeding surface–IL contact. This disrupts the templating effect of the surface on the IL,[23] and the strength of interfacial nanostructure is reduced. Further experiments using different salts and ILs are already underway to elucidate which of these factors is of greatest importance.

The force data provides no evidence of Li underpotential deposition, or gold dissolution due to the presence of chloride in the anodic regime, which has been reported in similar ILs at the Au(111) interface.[33] However, this cannot be excluded. Underpotential deposition would mean that a Li^+ cation attracted to the surface would not serve merely to balance the surface charge, but rather would be deposited and incorporated into the electrode. The form of the force data at −2.0 V and +2.0 V did not vary appreciably over the course of an experiment, which suggests that if underpotential deposition (or gold dissolution) is occurring it is not sufficiently rapid to significantly affect the Li^+ or Cl^- concentration appreciably. STM studies are currently underway that will resolve these issues. Nonetheless, these results demonstrate that interfacial IL nanostructure can be controlled *via* addition of low concentration of inorganic electrolyte, providing a simple method of tuning IL interfacial forces.

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